Chemical Physics 456 (2015) 8–12

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Concerted and asynchronous mechanism of ground state proton transfer in alcohol mediated 7-hydroxyquinoline

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ARTICLE INFO

Article history:
Received 14 February 2015
In final form 29 April 2015
Available online 9 May 2015

Keywords:
DFT
Concerted
Asynchronous
Proton transfer
7-Hydroxyquinoline

ABSTRACT

Alcohols mediated 7-hydroxyquinoline (7-HQ) complex has received enormous attractions on the issue of proton transfer reaction in the ground and excited states. In the present paper, concentrating on the ground state proton transfer (GSPT), density functional theory (DFT) calculations were carried out to investigate the intrinsic insight into the reaction mechanism. We found that the GSPT is concerted and asynchronous process and can be accelerated by more acidic alcohol. Such GSPT was initiated by the proton transfer from alcohol to keto group of 7-HQ and finished by the proton transfer from nitrogen to alcohol. Our findings were in agreement with experimental conclusions quite well. Our results would be helpful to understand the proton transfer reaction for 7-HQ and related systems.

1. Introduction

Proteins and their binding properties, especially at the center of intercellular signal transduction, control the functions of biological systems [1–3]. Many proteins have H-bonding networks mediated by solvent molecules to serve as proton transport, and prototropic reaction turns to play a crucial role in lots of reactions of chemical and biological processes [4–6]. Accordingly, mechanistic and dynamic studies on long-range proton relay in proteins are essential to understand the functions and the structural dynamics of proteins. In line with this context, it should be very interesting to study proton transfer through a proton wire, because many trans-membrane proteins create, control, or utilize proton gradients across biological membranes [7,8]. However, due to the structural complexity and the massive size of proteins, it is difficult to anatomize this process along a proton wire. Hence, it is necessary to establish a simplified model. In particular, aromatic molecular complexes involving polar molecules that can donate or accept a proton are quite attractive model systems. Extensive efforts have been focused on proton transport between aromatic molecules and small polar molecules [9–13]. One of the most frequently probed systems is 7-HQ complexed with solvent molecules.

During past two decades, extensive experimental and theoretical works were done to study 7-HQ complex, which is well known to undergo excited state proton transfer (ESPT) [14–21]. In normal condition, 7-HQ complex exists in the enol form complex (EC). After photo-excitation, EC was known to quickly transform to keto form complex (KC) via rapid intermolecular ESPT reaction [22–24]. Early in 1968, Mason et al. investigated photochemical properties of 7-HQ and pointed out that the OH group is more acidic and the ring N atom is more basic in the excited state than in the ground state [25]. Thistlethwaite et al. reported the picosecond fluorescence in methanol [26,27]. By monitoring the prominent fluorescence spectroscopy, Jang et al. observed the reaction rate of ESPT increases with the proton-donating ability of mediating alcohols, and proposed that ESPT takes place via two-step process [23,28–31]. By means of quantum simulations, we asserted a vibrational mode with low frequency to be the special one which can be impulsively excited during ESPT process [32].

Compared with fast ESPT, the slow GSPT reaction has been rarely revealed [33]. KC relaxes from the excited state to the ground state through irradiation, then recovers to EC again via GSPT reaction as illustrated in Scheme 1. Recently, Jang et al. observed, similarly to ESPT, the GSPT reaction can be accelerated by the proton donating ability of mediating alcohols [34]. It was further claimed that such GSPT reaction takes place asymmetrically by the initial and rate determining step of H3 tunneling to O3. Moreover, it was proposed that such GSPT reaction is concerted and asynchronous [34]. However, determining reaction synchronism is extremely hard for experiments, but feasible for computational calculations to obtain intrinsic insight. As we stated in a previous study [35], concerted/stepwise and synchronous/asynchronous are two different concepts. Concerted/stepwise means

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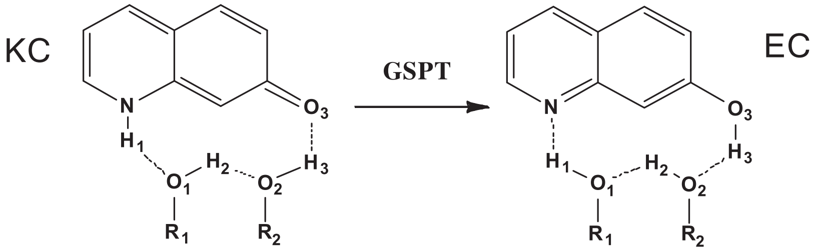
http://dx.doi.org/10.1016/j.chemphys.2015.04.016



Scheme 1. Illustration of GSPT reaction in alcohols mediated 7-HQ complex.

that the reaction takes place via single/multiple barrier without/with stable intermediates. However, synchronous process means that a chemical process takes place in a synchronous fashion. A concerted reaction is defined by Dewar as "a reaction that takes place in a single kinetic step without necessarily being synchronous" [36]. To achieve our goals, density function theory (DFT) calculations were carried out to study the corresponding structural and electronic properties in the ground state. We have validated the experimental hypothesis of such GSPT that GSPT in 7-HQ is concerted with three asynchronous steps.

2. Computational method

In this work, we employed first-principle calculations, through which we examined the GSPT reaction of 7-HQ complex with alcohols. DFT calculations were carried out using a suite of Gaussian 09 programs [37]. For DFT calculations, M06-2X exchange functional was known to provide excellent results for the combination of main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states [38–40]. Hence, we employed M06-2X functional to study GSPT reaction in current systems. The integral = ultrafine option was utilized to minimize the integration grid errors that may arise from using an inadequate grid in the current M06 suite of functionals. For a chemical reaction, solvent effects have an important influence on the potential energy barrier, enthalpy difference, and so on. In the present study, Tomasi's polarizable continuum model (PCM) by self-consistent reaction field (SCRF) method was utilized to investigate the solvent effect on the electron/proton transfer. In PCM model, the cavity was defined as the union of a series of interlocking atomic spheres. The polarization effect of the solvent continuum was computed by numerical integration [41], and n-heptane was chosen as the solvent in present paper because it was used in the experimental enviroment [34]. All the ground state geometries were fully optimized by the M06-2X with 6-311+G* basis set. The TS keyword was used to search transition states. The potential energy surfaces (PES) in the ground state was obtained along the proton transfer coordinates. The obtained geometries of saddle points along PES were confirmed to be local minima or transition states by frequency calculations at the same level of theory. The intrinsic reaction coordinate (IRC) calculations [42] were performed to confirm whether the TS connects to reactant and product. Frequency calculations were employed to analyze the vibrational mode, as well as to get the zero point energy (ZPE) correction. Unless mentioned otherwise, the energy differences and energy barriers reported here are ZPE corrected Gibbs free energies.

Once the activation barrier was obtained, the reaction rate constant can be approximately estimated by the following expression:

$$k(\mathrm{T}) = \frac{k_B T}{h} \exp\left(\frac{\Delta G^{+}}{RT}\right)$$

where k_B, T, h, ΔG^{+} and R are the Boltzmann constant, absolute temperature, Planck's constant, Gibbs activation energy ($G_{TS} - G_{RC}$), and gas constant. Here, the quantum tunneling factor was not included since it was reported to be very small at room temperature [43,44].

3. Results and discussion

First of all, the acidity of alchols and 7-HQ including enol monomer (EM) and keto monomer (KM) were approximately estimated by the energy of proton donation (E_{Don}), $E_{Don} = E_{Dep} - E_{Neu}$, where E_{Dep} and E_{Neu} stand for the energies of deprotonated and neutral form. Smaller E_{Don} implies stronger proton donating ability of alcohol. Here, methanol (Me), ethonal (Et) and tert-butanol (Bu) were chosen as mediating alcohols. As listed in Table 1, the acidity of the alcohol monomers is in the following order: Bu > Et > Me, which is different from experiment of Me > Et > Bu. The acidity reversal of simple alcohols from gas phase to bulk environment has been experimentally studied by Brauman and Blair [45,46]. In gas phase, increasing the number of alkyl substitutes can stablize negative charge and thus increases the alcohol acidity. Damraumer has computationally addressed the surrounding solvent effect on alcohol's acidity, and found that increasing surrounding solvent can reverse the order of simple alcohols' acidity [47]. Hence we characterized the proton donating ability by using alcohol dimer as target. As listed in Table 1, the order of alcohol dimer in acidity was Me > Et > Bu which is in line with experiment. Thus we used alcohol dimer as the mediating solvent molecules to facilitate proton transfer in 7-HQ complex. Moreover, surrounding environment little influences the acidity of EM and KM. Both EM and KM are more acidic than alcohols, with KM being the strongest, which is consistent with experiment [48].

KC was formed with two Me dimers through H-bonding as demonstrated in Scheme 1, and the optimized structure was shown in Fig. 1 (only the structure of active site was displayed, and the original structure is available in supporting information, Fig. S1). The bond length of H1—O1 (R_{H1-O1}) was 2.339 Å, and that of H2—O2 and H3—O3 (R_{H2-O2} and R_{H3-O3}) were 1.840 and 1.670 Å in KC. Due to H-bonding, bond lengths of N—H1, O1—H2 and O2—H3 (R_{N-H1}, R_{O1-H2} and R_{O2-H3}) were elongated to 1.016, 0.976 and 0.994 Å, respectively. After the triple proton transfer from KC, EC was produced and the obtained structure was shown in Fig. 1. In EC, R_{H1-O1}, R_{H2-O2} and R_{H3-O3} were 0.978, 0.979 and 0.975 Å, and R_{N-H1}, R_{O1-H2} and R_{O2-H3} were 1.945, 1.805 and 1.895 Å, respectively. Frequency calculations confirmed that both KC and EC were local minima since no imaginary vibrational mode was observed. Based on fully optimized KC and EC, transition state (TS) was sought by TS keyword. In TS, as shown in Fig. 1, H1 moved slightly with R_{N-H1}/R_{H1-O1} of 1.079/1.604 Å, H3 was bound to O3

Table 1
Estimated proton donating energy of alcohol and isolated 7-HQ monomers (in the unit of eV).

		Me	Et	Bu	EM	KM
E_{Don}	Monomer	12.80	12.73	12.63	11.30	10.88
	Dimer	14.27	14.29	14.36		